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**Polyester Resin Composition for Calendering
and Sheet Obtained Using This Composition**

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(54) [Title of the Invention]

Polyester Resin Composition for Calendering
and Sheet Obtained Using This Composition

(57) [Summary]

[Object] To provide a polyester resin composition that has exceptional roll release properties when calendered, yields good transparency in finished sheet, and enables calendered sheet to have exceptional levels of quality in terms of solvent and detergent resistance.

[Means of Achievement] The aforementioned objective is achieved by means of using a polyester resin composition for calendering that comprises (a) 30 to 97 weight parts of amorphous polyester, (b) 3 to 70 weight parts of crystalline polyester, (c) 0.1 to 10 weight parts of a crystal-nucleating agent, and (d) 0.01 to 5 weight parts of a lubricant.

[Claims]

[Claim 1] A polyester resin composition for calendering, characterized by containing (a) an amorphous polyester resin, (c)* a crystal-nucleating agent, and (d) a lubricant.

[Claim 2] The polyester resin composition for calendering according to Claim 1 containing at least two polyesters, (c)* a crystal-nucleating agent, and (d) a lubricant, said polyester resin composition for calendering being characterized in that at least one of the two or more polyesters is amorphous polyester (a).

[Claim 3] The polyester resin composition for calendering according to Claim 2, characterized in comprising (a) an amorphous polyester, (b) a crystalline polyester, (c) a crystal-nucleating agent, and (d) a lubricant, and comprising 30 to 97 weight parts of (a), 3 to 70 weight parts of (b), 0.1 to 10 weight parts of (c), and 0.01 to 5 weight parts of (d), based on a total of 100 weight parts for (a) and (b) components.

[Claim 4] The polyester resin composition for calendering according to Claims 1 to 3, characterized in that amorphous polyester (a) has as principal components an aromatic dicarboxylic acid having 8 to 14 carbons and either an aliphatic or alicyclic glycol having 2 to 10 carbons.

[Claim 5] The polyester resin composition for calendering according to Claim 4, characterized in that the aromatic dicarboxylic acid having 8 to 14 carbons of amorphous polyester (a) is either terephthalic acid or isophthalic acid.

* [Translator's note: the Japanese sequence literally jumps to "(c)" without specifying "(b)", but in later claims a component "(b)" is also included.]

[**Claim 6**] The polyester resin composition for calendering according to Claims 4 or 5, characterized in that the aliphatic or alicyclic glycol having 2 to 10 carbons of amorphous polyester (a) is ethylene glycol, diethylene glycol, neopentyl glycol, or cyclohexane dimethanol.

[**Claim 7**] The polyester resin composition for calendering according to Claims 3 to 6, characterized in that the melting point of crystalline polyester (b) is 90 to 220°C.

[**Claim 8**] The polyester resin composition for calendering according to Claims 3 to 7, characterized in containing 50 mol% or more of at least one compound from among 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and cyclohexane dimethanol when the total glycol component of crystalline polyester (b) is 100 mol%.

[**Claim 9**] The polyester resin composition for calendering according to Claims 1 to 8, characterized in that a metal salt of an organophosphate ester is used as the lubricant.

[**Claim 10**] The polyester resin composition for calendering according to Claims 1 to 9, characterized in that the tensile storage modulus at 25°C is 1×10^7 Pa or higher, and the temperature region in which the tensile storage modulus ranges from 1×10^7 Pa to 1×10^6 Pa is 60°C or higher.

[**Claim 11**] Sheet obtained by means of calendering the resin composition of Claims 1 to 10.

[Detailed Description of the Invention]

[0001]

[**Technological Field of the Invention**] The present invention relates to a readily calenderable polyester resin composition that has exceptional roll release properties, long-run workability, and thermostability when polyester calendering is performed, and that may be used in shrink labels for foodstuffs, cosmetics, and beverages; aroma-retaining heat-seal films; oil-resistant multilayered sheet; or other various sheet/film configurations, and particularly in industrially machined sheet/film.

[0002]

[**Prior Art**] Vinyl chloride ("VC" hereunder) sheet (and film) is inexpensive and has exceptional transparency, which have conventionally led such materials to be extensively used in a variety of applications. Methods known in the art for working such sheets include extrusion molding and calender molding; however, friction at the die tip will alter the workability (moldability) of the

resin in extrusion molding, leading to greater inaccuracy with respect to such factors of the sheet (film) as thickness, width, and direction of travel, and reduced suitability to mass production, as compared to calender molding. Accordingly, the latter method is more widely used when productivity and quality are required. Furthermore, the flexibility of VC may be easily adjusted through the addition of a plasticizer, thereby facilitating the working of the sheet; a typical example of application is decorative sheet (film) imprinted with a wood grain to lend the appearance of a wooden article. However, concerns relating to dioxin emissions when vinyl chlorides are incinerated, as well as to controls on the use of plasticizers, which are endocrine disrupting substances, have prompted action in recent years to use alternative materials in place of VC sheet (film). Polyester is valued over a number of substitute materials due in part to its physical properties and cost; however, the two major problems below are encountered when using polyester as substitutes.

[0003] The first problem is that polyester is poorly suited to calender molding, which is extensively used as a method for molding VC sheet. Ease of workability has been the reason extrusion molding has been extensively used as a method for manufacturing sheet and film from polyester resins. When such polyester resins are calendered, however, relatively strong adhesive forces are encountered with the rolls during thermoplasticization, and the resins tend to adhere to the rolls, which complicates the molding procedure. Attempts have been made to add a variety of lubricants to prevent the resin from adhering to the rolls. Lubricants based on polyethylene waxes, paraffin wax, and other various hydrocarbons; higher fatty acids; higher alcohols; fatty acid amides; and esters, as well as metallic soaps based on higher fatty acids and other materials have all been attempted, but adequate roll release properties and long-run work times have been unobtainable, and the resulting sheet (film) suffers coloration under long-run working, thereby producing a poor color tone.

[0004] The second problem occurs when amorphous polyester or high-transparency crystalline polyester is employed in order to obtain transparent sheet, and concerns the low resistance provided against reagents such as solvents or detergents, and to whitening or swelling occurring as a result of immersing or rubbing the sheet. Dirt frequently adheres to decorative sheet laminated with wooden materials that are fashioned into articles such as tables and compartment doors for household furniture or sink units. Using a solvent such as alcohol or methyl ethyl ketone to wipe the dirt off will whiten, swell, or dissolve the polyester on the surface, thereby

degrading the appearance of the article, and making it unusable. A household or kitchen detergent is commonly used to remove dirt from articles of furniture used in a normal domestic setting, but the same problem with degraded appearance will be countered as when a solvent is used to wipe off the object.

[0005] Conventional examples in which calendering was attempted with polyester resin are provided below, and further detail is also provided with regard to the prior art. Sheets have been obtained in Japanese Laid-Open Patent Application (Kokai) Nos. 7-278418 and 8-283547 by means of calendering crystalline polybutylene terephthalate-based elastomers, but the resin became crystallized directly after being worked, and the sheet became whitened, thereby precluding its use in decorative sheet applications where transparency is required. In US Patent No. 6068910 and Japanese Patent Application (Kokai) Laid Open Nos. 11-343353, 2000-136294, 2000-186191, 2000-302951, 2001-64496, and 2001-4019, sheets have been obtained by means of calendering crystalline polyethylene terephthalate that has been copolymerized with cyclohexane dimethanol. Although good transparency was obtained, solvent resistance was inadequate in all cases, causing the sheet to whiten when immersed in solvents, and obviating any practical application as decorative sheet. Calendering was performed using a lubricant in a test that has been disclosed by the present inventors, as a result of which the transparency and printability of the calendered sheet were diminished when larger amounts of lubricant were used, and the roll release properties during calendering were diminished when smaller amounts of lubricant were used. A good balance between the two could not be attained. When these lubricants were the principal components, moreover, the sheet gradually suffered coloration under long-run working, and its appearance deteriorated.

[0006]

[Problems Intended to Be Resolved by the Invention] With the foregoing issues in view, it is an object of the present invention to provide a polyester resin composition for calendering that establishes a balance between the roll release properties during calendering and the attributes of the worked sheet (i.e., provides virtually no coloring, good transparency and printability, and exceptional resistance to solvents and detergents).

[0007]

[Means Used to Solve the Above-Mentioned Problems] The present inventors conducted diligent investigations in an attempt to achieve the aforementioned object, and perfected the present invention based on the discovery that the compounding of an amorphous polyester, crystalline polyester resin, crystal-nucleating agent, and lubricant serves to establish a balance between the roll release properties and long-run workability during calendering, and the attributes of the worked sheet (i.e., provides virtually no coloring, good transparency and printability, and exceptional resistance to solvents and detergents).

[0008] In other words, the present invention has the characteristics described hereunder.

(1) A polyester resin composition for calendering, characterized by containing (a) an amorphous polyester resin, (c)* crystal-nucleating agent, and (d) lubricant.

[0009] (2) The polyester resin composition for calendering according to (1) above, containing at least two polyesters, (c)* a crystal-nucleating agent, and (d) lubricant, with the polyester resin composition for calendering being characterized in that at least one of the two or more polyesters is amorphous polyester (a).

[0010] (3) The polyester resin composition for calendering according to (2) above, characterized in comprising (a) an amorphous polyester, (b) crystalline polyester, (c) crystal-nucleating agent, and (d) lubricant, and comprising 30 to 97 weight parts of (a), 3 to 70 weight parts of (b), 0.1 to 10 weight parts of (c), and 0.01 to 5 weight parts of (d) based on a total of 100 weight parts for (a) and (b) components.

[0011] (4) The polyester resin composition for calendering according to (1) or (2) above,** characterized in that amorphous polyester (a) has as principal components an aromatic dicarboxylic acid having 8 to 14 carbons and either an aliphatic or alicyclic glycol having 2 to 10 carbons.

[0012] (5) The polyester resin composition for calendering according to (4) above, characterized in that the aromatic dicarboxylic acid having 8 to 14 carbons of amorphous polyester (a) is either terephthalic acid or isophthalic acid.

* [Translator's note: here and elsewhere please refer to the earlier note regarding component "(c)."]

** [Translator's note: please note that reference is made only to items (1) and (2) here, as opposed to Claim (4), which is the equivalent of paragraph (0011), and which references (1) to (3). All of the other claim restatements cited in paras (0008) to (0017) are consistent with the corresponding references cited in the actual Claims themselves.]

[0013] (6) The polyester resin composition for calendering according to (4) or (5) above, characterized in that the aliphatic or alicyclic glycol having 2 to 10 carbons of amorphous polyester (a) is ethylene glycol, diethylene glycol, neopentyl glycol, or cyclohexane dimethanol.

[0014] (7) The polyester resin composition for calendering according to (3) to (6) above, characterized in that the melting point of crystalline polyester (b) is 90 to 220°C.

[0015] (8) The polyester resin composition for calendering according to (3) to (7) above, characterized in containing 50 mol% or more of at least one compound from among 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and cyclohexane dimethanol when the total glycol component of crystalline polyester (b) is 100 mol%.

[0016] (9) The polyester resin composition for calendering according to (1) to (8) above, characterized in that a metal salt of an organophosphate ester is used as the lubricant.

[0017] (10) The polyester resin composition for calendering according to (1) to (9) above, characterized in that the tensile storage modulus at 25°C is 1×10^7 Pa or higher, and the temperature region in which the tensile storage modulus ranges from 1×10^7 Pa to 1×10^6 Pa is 60°C and higher.

(11) Sheet obtained by means of calendering the resin composition of (1) to (10) above.

[0018]

[Embodiments of the Invention] The polyester resin composition for calendering of the present invention comprises (a) an amorphous polyester resin, (c) crystal-nucleating agent, and (d) lubricant. The term "amorphous" shall have the following connotation in the present invention. Specifically, using a differential scanning calorimeter (DSC), the temperature is elevated from -100°C to 300°C at a rate of 20°C/min, then reduced from 300°C to -100°C at a rate of 50°C/min, and subsequently elevated once more from -100°C to 300°C at a rate of 20°C/min. The product is amorphous if no distinct fusion peaks appear in either of the temperature elevation processes. Conversely, "crystalline" refers to a distinct fusion peak appearing when measurements are taken using a DSC under similar conditions. At least two types of polyester are preferably contained in the polyester resin composition of the present invention in order for a balance between the roll release properties and the attributes of the worked sheet to be established to a high level, with at least one of the polyesters being amorphous polyester. It is

further preferred for the resin composition to contain (b) a crystalline polyester in addition to the amorphous polyester.

[0019] Amorphous polyester resin (a), crystal-nucleating agent (c), and lubricant (d) are contained in the present invention as essential components. Contact with a solvent will prompt crystallization and whitening to occur, even if the polyester exhibits no distinct peak when DSC is performed. Adding the crystal-nucleating agent is believed to have the effect of forming crystals that are sufficiently small to have no adverse effect on the transparency of the sheet itself. The presence of the crystalline component is believed to inhibit molecular motion and to prevent whitening without causing any swelling in the resin even if a solvent has adhered to the sheet surface; however, this reason shall not in any circumstance be used to establish the scope of patent rights.

[0020] A lubricant is an essential component for preventing the polyester resin from adhering to the calender rolls. At least two polyesters are preferably used in the present invention to further enhance this effect, with at least one of the two or more polyesters being amorphous polyester (a). Of the two or more types of polyester, those that are more apt to crystallize are believed to undergo rapid crystallization to an extent that does not detract from transparency. Adding crystalline polyester (b) is preferred. The crystalline polyester present in the finished sheet is believed to crystallize to the extent to which the transparency of the sheet as such is not compromised in order to bring out the solvent properties.

[0021] A description of the polyesters shall now be provided. The lower limit of the amount of amorphous polyester (a) to be compounded per 100 weight parts of the polyester of the present invention is 30 weight parts, preferably 50 weight parts, and ideally 65 weight parts, while the upper limit is preferably 97 weight parts, and ideally 90 weight parts. The lower limit of crystalline polyester (b) to be compounded is preferably 3 weight parts, and ideally 5 weight parts, while the upper limit is preferably 70 weight parts, more preferably 50 weight parts, and ideally 35 weight parts. The amount of amorphous polyester compounded is preferably not less than 30 weight parts, due to the difficulty in adjusting the viscoelasticity at the working temperature, which is done to prevent the resin from sagging during calendering, and due to the whitened appearance in the finished sheet arising from a high level of crystallinity. Conversely, if the amount of amorphous polyester compounded exceeds 97 weight parts, the solvent

resistance and detergent resistance of the finished sheet will be difficult to maintain at high levels.

[0022] It is desirable for amorphous polyester resin (a) used in the present invention to have as principal components therein an aromatic dicarboxylic acid having 8 to 14 carbons and either an aliphatic or alicyclic glycol having 2 to 10 carbons. A "principal component" herein is considered to comprise 50 mol% or more, preferably 60 mol% or more, and more preferably 65 mol% or more of each of the acid and glycol components when the total quantity of the acid and glycol component is taken to be 100 mol%. If the amount of each component is less than 50 mol%, the elongation and mechanical properties of the calendered sheet will be diminished.

[0023] The aromatic dicarboxylic acid having 8 to 14 carbons in amorphous polyester resin (a) used in the present invention is desirably terephthalic acid or isophthalic acid. Using these dicarboxylic acids will further enhance the elongation and mechanical properties of the calendered sheet.

[0024] Polycarboxylic acids other than terephthalic acid and isophthalic acid may be alternatively copolymerized with amorphous polyester resin (a) of the present invention. Examples of acids that are well known in the art include orthophthalic acid, naphthalenedicarboxylic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, decanoic acid, dimer acids, cyclohexanedicarboxylic acid, and trimellitic acid.

[0025] The aliphatic or alicyclic glycol having 2 to 10 carbons in amorphous polyester (a) used in the present invention is preferably ethylene glycol, diethylene glycol, neopentyl glycol, or cyclohexane dimethanol. It is moreover preferable to have ethylene glycol contained as an essential component in an amount of 40 mol% or more, even 50 mol% or more, and in particular 4 mol% [sic] or more; and at least one compound selected from among diethylene glycol, neopentyl glycol, and cyclohexane dimethanol contained in an amount of less than 60 mol%, more preferably less than 50 mol%, and in particular less than 40 mol%. At least one compound selected from among diethylene glycol, neopentyl glycol, and cyclohexane dimethanol is preferably contained in an amount of 10 mol% or more, and in particular 15 mol% or more. Combinations of ethylene glycol and neopentyl glycol have good affinity with lubricants, and readily establish a balance between the roll release properties and sheet transparency.

[0026] Amorphous polyester resin (a) of the present invention may be copolymerized with a polyhydric alcohol component different from the aforementioned ethylene glycol, diethylene

glycol, neopentyl glycol, or cyclohexane dimethanol, with relevant examples including 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 2-methyl-1,3-propanediol, hexane diol, nonane diol, dimer diol, ethylene oxide adducts or propylene oxide adducts of bisphenol A, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, 2-butyl-2-ethyl-1,3-propanediol, tricyclodecane dimethanol, neopentyl hydroxypivalic ester, 2,2,4-trimethyl-1,5-pentanediol, and trimethylol propane.

[0027] The melting point of crystalline polyester resin (b) used in the present invention is preferably 90 to 220°C. A lower limit of 100°C is even more preferable, while 110°C is ideal. A preferable upper limit is 200°C, while 190°C is ideal. If the melting point is less than 90°C, the crystallinity will decrease, which will diminish the solvent resistance and detergent resistance. On the other hand, if the melting point is higher than 220°C, the surface temperature of the rolls will need to be increased during calendering, which will reduce the molecular weight of the polyester due to hydrolysis. Accordingly, poor roll release properties will be obtained during working, and sheet elongation will decrease.

[0028] When the total glycol component is 100 mol%, the crystalline polyester (b) used in the present invention will preferably contain 50 mol% or more of at least one compound from among ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and cyclohexane dimethanol. A content of 55 mol% or more is more preferable, with 60 mol% or more being ideal. The crystalline polyester present in the sheet must crystallize rapidly in order for solvent resistance to be exhibited, and the aforementioned components are preferably contained in an amount of 50 mol% or more in order for adequate crystallinity to be imparted. Conversely, solvent resistance will diminish if the amount is less than 50 mol%. Crystallization proceeds relatively rapidly in particular with ethylene glycol, 1,3-propanediol, and 1,4-butanediol, which makes these compounds preferred among the aforementioned components from the perspective of solvent resistance.

[0029] Crystalline polyester (b) used in the present invention may be copolymerized with a polycarboxylic acid or polyhydric alcohol that is different from ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and cyclohexane dimethanol as described in the foregoing. Examples of polycarboxylic acids that are well known in the art include terephthalic acid, isophthalic acid, orthophthalic acid, naphthalenedicarboxylic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, decanoic acid, dimer acids, cyclohexanedicarboxylic acid, and

trimellitic acid. Examples of polyhydric alcohols that are well known in the art include 1,2-butanediol, 1,3-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 2-methyl-1,3-propanediol, nonane diol, dimer diol, ethylene oxide adducts or propylene oxide adducts of bisphenol A, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, 2-butyl-2-ethyl-1,3-propanediol, tricyclodecane dimethanol, neopentyl hydroxypivalic ester, 2,2,4-trimethyl-1,5-pentanediol, and trimethylol propane.

[0030] The number-average molecular weight of the amorphous polyester resin (a) and crystalline polyester resin (b) used in the present invention is preferably 15000 to 40000, more preferably 18000 to 35000, and ideally 20000 to 35000. If the number-average molecular weight is less than 15000, the strength and elongation of the sheet is inadequate, due to inadequate resin cohesion, which makes it brittle and unusable. On the other hand, because the melt viscosity rises if the number-average molecular weight is 40,000 or above, the optimal temperature for calendering also rises, which results in poor roll release properties in the sheet.

[0031] The acid value of amorphous polyester resin (a) and crystalline polyester resin (b) used in the present invention is preferably $100 \text{ eq}/10^6 \text{ g}$ or less, more preferably $50 \text{ eq}/10^6 \text{ g}$ or less, and ideally $40 \text{ eq}/10^6 \text{ g}$ or less. If the acid value exceeds $100 \text{ eq}/10^6 \text{ g}$, hydrolysis will accelerate when the resin is heated during calendering, and the mechanical strength of the finished sheet will decrease. Moreover, the roll release properties will diminish as the resin decomposition proceeds.

[0032] The melt viscosity of the polyester resin composition used in the present invention is preferably 6000 to 60000 dPa • sec, more preferably 7000 to 50000 dPa • sec, and ideally 8000 to 40000 dPa • sec when the shear rate is 100 sec^{-1} at a temperature of 220°C . If the melt viscosity is less than 6000 dPa • sec, the adhesiveness of the resin will increase, and the roll release properties will diminish. On the other hand, a melt viscosity greater than 60000 dPa • sec will be excessively high, and will prevent a practical degree of productivity from being attained.

[0033] Crystal-nucleating agent (c) must also be added into the polyester resin composition of the present invention. The lower limit of the amount of the crystal-nucleating agent to be compounded per 100 weight parts of the total polyester resin is 0.1 weight parts, and the upper limit is 10 weight parts. The lower limit is preferably 0.5 weight parts, and the upper limit 5 weight parts. If the amount to be compounded is less than 0.1 weight parts, diminished solvent resistance will result, while if the amount exceeds 10 weight parts, the flowability during

calendering and the mechanical properties of the sheet will decrease, neither of which is preferable. The crystal-nucleating agent increases the crystallization rate of the crystalline polyester, enhances the orientation of the amorphous polyester, allows crystallization and orientation to be rapidly concluded, and makes it possible to control the size of the spherulites by means of adjusting the number of crystal nuclei. As long as the resulting spherulites are extremely fine crystals whose diameters are the same or less than the wavelength of visible light, it is believed that no loss in transparency will be experienced, even after the resin has crystallized, and a balance between the transparency and solvent resistance of the sheet may be readily achievable.

[0034] The spherulites have diameters of 300 nm or less, 200 nm or less, and especially 100 nm or less, in increasing order of preference. Specific examples of crystal-nucleating agents include talc; silica; graphite; carbon powder; pyrophyllite; gypsum; neutral clay and other inorganic fine particles; magnesium oxide, aluminum oxide, titanium dioxide, and other metal oxides; sulfates; phosphates; silicates; oxalates; stearates; benzoates; salicylates; tartrates; sulfonates; montanic acid wax salts; montanic acid wax ester salts; terephthalates; carboxylates; and ionic copolymers comprising α -olefins and α,β -unsaturated carboxylic acids. Especially effective among these materials are oxalates, stearates, benzoates, salicylates, tartrates, sulfonates, montan wax salts, montan wax ester salts, terephthalates, carboxylates, and α -olefins. Among the aforementioned salts, alkali metal salts, and sodium salts in particular, are highly effective in reducing the size of the crystal nuclei, and are accordingly preferred.

[0035] A lubricant must be compounded with the polyester resin of the present invention in order for improved roll release properties to be realized when the resin is calendered to fabricate a sheet.

[0036] The amount of the lubricant used in the present invention to be compounded is 0.01 to 5 weight parts per 100 weight parts of the total polyester resin. The lower limit is preferably 0.05 weight parts, more preferably 0.1 weight parts, and ideally 0.5 weight parts, while the upper limit is preferably 4.5 weight parts, more preferably 4 weight parts, and ideally 3.5 weight parts. If the amount of lubricant is less than 0.01 weight parts, the effect of improving the roll release properties will be difficult to attain, while if the amount exceeds 5 weight parts, diminished transparency, coloration, and printability of the worked sheet will tend to occur.

[0037] Examples of the lubricant used in the present invention include polyolefinic waxes, metal salts of organophosphate esters, organophosphate esters, ester compounds of higher aliphatic alcohols and either adipic acid or azelaic acid, ethylene bisstearamide, methylene bisstearamide, glycerine higher fatty acid ester compounds, pentaerythritol higher fatty acid ester compounds, higher aliphatic alcohols, higher fatty acids, petroleum- or coal-derived paraffins, waxes, natural or synthetic polymer ester waxes, and metallic soaps made from higher fatty acids. The aforementioned lubricants may be used individually or in combinations of two or more. The use of a polyolefinic wax and/or a metal salt of an organophosphate ester is particularly preferred.

[0038] Examples of polyolefinic waxes used as a lubricant in the present invention include polyethylene waxes, polypropylene waxes, and derivatives thereof. Examples of such derivatives include copolymers with other monomers such as acrylic acid, vinyl acetate, styrene, and maleic acid, and partially oxidized decomposition products.

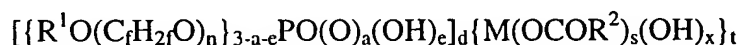
[0039] Examples of metal salts of organophosphate esters used as a lubricant in the present invention include metal salts of organophosphate esters expressed by general formula (I) below and/or metal salts of organophosphate esters expressed by general formula (II) below.

[0040] Formula (1):



(wherein R is a hydrocarbon group having 4 to 30 carbons; M is an alkali metal, alkaline-earth metal, zinc, or aluminum; a is 1 or 2; e is 0 or 1 (but 0 or 1 when a is 1, and 0 when a is 2); b is 0 to 2; c is 1 or 2; d is 1 to 3; f is 2 or 3; n is 0 to 60; and a, b, c, and d have the following relationship with the valence (hereunder indicated as m) of the metal (M): when m = 1, then b = 0, d = 1, and a = c; when m is 2, then b = 0, c = 1, and a × d = 2, or b = 1, d = 1, and a = c; when m = 3, then b = 0, d = 3, a = c, b = 1, c = 1, and a × d = 2, or b = 2, d = 1, and a = c; and when m ≥ 2, mutually different phosphate ion groups may also be bonded to the metal (M), in which case d = 2 or 3 is the total number of phosphate ion groups that are mutually different. Further, when d is 2 or 3, the respective structures in brackets may be the same or different from each other.)

[0041] Formula (II):



* [Translator's note: the "o" in the subscripted "3-a-o" may be a typographical error, since no explanation is provided for that symbol in the description following the formula. It is likely to be "e."]

(wherein R^1 is a hydrocarbon group having 4 to 30 carbons; R^2 is an alkyl group having 1 to 25 carbons; M is an alkali metal, alkaline-earth metal, zinc, or aluminum; a is 1 or 2; e is 0 or 1 (but is 0 or 1 when a is 1, and is 0 when a is 2); d = 1 or 2; s is 1 or 2; x is 0 or 1; t is 1 or 2; f is 2 or 3; and n is 0 to 60. $s + x = 1$ or 2, and a, d, s, and t have the following relationship with the valence (hereunder indicated as m) of the metal (M): when $m = 2$, then $s = 1$, $d = 1$, and $a = t$; when $m = 3$, then $s = 1$, $t = 1$, and $a \times d = 2$, or $s = 2$, $d = 1$, and $a = t$; and when $m = 3$, mutually different phosphate ion groups may be bonded with the metal (M), in which case $d = 2$ signifies the total number of phosphate ion groups. Furthermore, when d is 2, the respective structures in brackets may be the same or different from each other.)

[0042] Alkyl groups, phenyl groups, arylalkyl groups, alkenyl groups, or alkyl phenyl groups are preferred as the hydrocarbon groups having 4 to 30 carbons indicated by R in general formula (I) and as the hydrocarbon groups having 4 to 30 carbons indicated by R^1 in general formula (II). Preferred examples of the alkali metals that are represented by M in general formula (I) and general formula (II) include lithium, sodium, and potassium, and preferred examples of the alkaline-earth metals include magnesium, calcium, and barium.

[0043] The metal salts of the organophosphate esters expressed by general formula (I) and the metal salts of the organophosphate esters represented by general formula (II) may be manufactured by means of common methods, and there are no particular limitations as regards to such methods of manufacture.

[0044] Preferred examples of the metal salts of the organophosphate esters represented by general formula (I) include compounds (1) to (13) in Table 1 below and compounds (14) to (16) in Table 2 below. Preferred examples of the metal salts of the organophosphate esters represented by general formula (II) include compounds (15) to (26) in Table 2 below. These compounds may be used individually or in combinations of two or more.

[0045] Also, as shown by decimal fractions included in the number of repetitions of oxyethylene or oxytrimethylene units in the polyether alcohol component, these compounds (compounds (1) through (26)) are pure compounds or mixtures of a plurality of metal salts of phosphate esters having different numbers of repeating oxyethylene units or oxytrimethylene units in the polyether alcohol component (the number of repetitions (n) in $(C_1H_{21}O)_n$ in the formula).

[0046]

[Table 1]

| Cpd no. | Structural formula | Cpd no. | Structural formula |
|---------|---|---------|---|
| (1) | $C_{10}H_{23}-(OCH_2CH_2)_{3.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(ONa)$ | (8) | $[C_{20}H_{41}-(OCH_2CH_2)_{10.5}-O]_2-P(=O)(OH)-ZnOH$ |
| (2) | $C_8H_{17}-(OCH_2CH_2)_{20.5}-O-\overset{\overset{O}{\parallel}}{P}(OLi)_2$ | (10) | $[C_{20}H_{41}-(OCH_2CH_2)_{10.5}-O]_2-P(=O)(OH)-O-\overset{\overset{O}{\parallel}}{P}(OH)_2$ $C_{20}H_{41}-(OCH_2CH_2)_{4.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)_2$ |
| (3) | $C_{10}H_{21}-(OCH_2CH_2)_{16.5}-O-\overset{\overset{O}{\parallel}}{P}(OCa)_2$ | | |
| (4) | $C_{13}H_{27}-(OCH_2CH_2)_{6.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(OMgOH)$ | (11) | $[C_{10}H_{21}-(OCH_2CH_2)_{10.5}-O]_2-P(=O)(OH)-O-\overset{\overset{O}{\parallel}}{P}(OH)(Mg)$ $C_{10}H_{21}-(OCH_2CH_2)_{4.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(Mg)$ |
| (5) | $C_{14}H_{29}-(OCH_2CH_2)_{4.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(OCa)$ | | |
| (6) | $[C_{12}H_{25}-(OCH_2CH_2)_{7.5}-O]_2-P(=O)(OK)$ | | |
| (7) | $[C_{12}H_{25}-(OCH_2CH_2)_{11.5}-O]_2-P(=O)(Zn)$ | (12) | $C_{10}H_{25}-(OCH_2CH_2)_{5.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(OLi)$ |
| (8) | $C_{13}H_{27}-(OCH_2CH_2)_{8.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(Zn)$ | (13) | $C_6H_5-(OCH_2CH_2)_{4.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(OH)$ |

[0047]

[Table 2]

| Cpd no. | Structural formula | Cpd no. | Structural formula |
|---------|---|---------|--|
| (14) | $C_{10}H_{23}-(OCH_2CH_2CH_2)_{3.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(ONa)$ | (21) | $C_{12}H_{25}-(OCH_2CH_2)_{6.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(O-C_6H_5)$ |
| (15) | $[C_6H_5-(OCH_2CH_2)_{12}-O]_2-P(=O)(OCa)_2$ | (22) | $[C_{12}H_{25}-(OCH_2CH_2)_{9.5}-O]_2-P(=O)(OH)-O-C_6H_5$ |
| (16) | $C_{21}H_{43}-O-\overset{\overset{O}{\parallel}}{P}(OH)(Zn)$ | (23) | $[C_{10}H_{21}-(OCH_2CH_2)_{8.5}-O]_2-P(=O)(OH)-O-C_6H_5$ |
| (17) | $C_{14}H_{29}-(OCH_2CH_2)_{7.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(OCa)$ | (24) | $C_6H_5-(OCH_2CH_2)_{10.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(OCa)$ |
| (18) | $C_9H_{19}-(OCH_2CH_2)_{3.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(Mg)$ | (25) | $C_{10}H_{21}-(OCH_2CH_2CH_2)_{11.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(OCa)$ |
| (19) | $C_8H_{17}-(OCH_2CH_2)_{18.5}-O-\overset{\overset{O}{\parallel}}{P}(OH)(OCa)$ | (26) | $[C_{12}H_{25}-(OCH_2CH_2)_{12}-O]_2-P(=O)(OH)-O-C_6H_5$ |
| (20) | $[C_{12}H_{25}-(OCH_2CH_2)_{20.5}-O]_2-P(=O)(OH)-O-C_6H_5$ | | |

[0048] It is desirable for the polyester resin of the present invention to be used as a composition into which an antioxidant has been admixed, in order to prevent heat degradation of the polyester resin during working (i.e., to prevent heat degradation from coloring the resin or making it adhere to the rolls). Examples of preferred antioxidants include phenolic antioxidants and organophosphite ester compounds.

[0049] Specific examples of phenolic antioxidants to be used in the present invention include 2,6-di-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol, 2,6-di-*tert*-butyl-4-ethylphenol, 2-*tert*-butyl-4,6-dimethylphenol, 2,4,6-tri-*tert*-butylphenol, 2-*tert*-butyl-4-methoxyphenol, 3-methyl-4-isopropylphenol, 2,6-di-*tert*-butyl-4-hydroxymethylphenol, 2,2-*bis*(4-hydroxyphenyl)propane, *bis*(5-*tert*-butyl-4-hydroxy-2-methylphenyl)sulfide, 2,5-di-*tert*-amylhydroquinone, 2,5-di-*tert*-butylhydroquinone, 1,1-*bis*(3-*tert*-butyl-4-hydroxy-5-methylphenyl)butane, *bis*(3-*tert*-butyl-2-hydroxy-5-methylphenyl)methane, 2,6-*bis*(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)-4-methylphenol, *bis*(3-*tert*-butyl-4-hydroxy-5-methylbenzyl)sulfide, *bis*(3-*tert*-butyl-5-ethyl-2-hydroxyphenyl)methane, *bis*(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane, *bis*(3-*tert*-butyl-2-hydroxy-5-methylphenyl)sulfide, 1,1-*bis*(4-hydroxyphenyl)cyclohexane, ethylene*bis*[3,3-*bis*(3-*tert*-butyl-4-hydroxyphenyl)butyrate], *bis*[2-(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)-4-methyl-6-*tert*-butylphenyl]terephthalate, 1,1-*bis*(2-hydroxy-3,5-dimethylphenyl)-2-methylpropane, 4-methoxyphenol, cyclohexylphenol, *p*-phenylphenol, catechol, hydroquinone, 4-*tert*-butylpyrocatechol, ethyl gallate, propyl gallate, octyl gallate, lauryl gallate, cetyl gallate, β -naphthol, 2,4,5-trihydroxybutyrophenone, *tris*(3,5-di-*tert*-butyl-4-hydroxyphenyl)isocyanate, 1,3,5-trimethyl-2,4,6-*tris*(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene, 1,6-*bis*[2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxy] hexane, *tetrakis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxymethyl]methane, *bis*(3-cyclohexyl-2-hydroxy-5-methylphenyl)methane, *bis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxyethyl]sulfide, *n*-octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, *bis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionylamino] hexane, 2,6-*bis*(3-*tert*-butyl-2-hydroxy-5-methylphenyl)-4-methylphenol, *bis*[S-(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)]thioterephthalate, *tris*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxyethyl]isocyanurate, *tris*(3,5-di-*tert*-butyl-4-hydroxybenzyl) isocyanurate, and 1,1,3-*tris*(3-*tert*-butyl-4-hydroxy-6-methylphenyl)butane. These compounds may be used individually or in combinations of two or more.

[0050] The upper limit of the amount of the phenolic antioxidant to be compounded is preferably 1.0 parts by weight or less, and especially preferably 0.8 parts by weight or less. The lower limit is preferably 0.01 parts by weight or greater, and especially preferably 0.02 parts by weight or greater. If the amount to be compounded is less than 0.01 parts by weight, the effect of inhibiting heat degradation during working will become difficult to obtain. If the amount exceeds 1.0 parts by weight, the effects that minimize heat degradation will be excessive, which is not economically advantageous.

[0051] Specific examples of organophosphite ester compounds include triphenyl phosphite, *tris*(methylphenyl) phosphite, triisooctyl phosphite, tridecyl phosphite, *tris*(2-ethylhexyl) phosphite, *tris*(nonylphenyl) phosphite, *tris*(octylphenyl) phosphite, *tris*[decylpoly(oxyethylene)] phosphite, *tris*(cyclohexylphenyl) phosphite, tricyclohexyl phosphite, tri(decyl) thiophosphite, triisodecylthiophosphite, phenyl · *bis*(2-ethylhexyl) phosphite, phenyl · diisodecyl phosphite, tetradecylpoly(oxyethylene) · *bis*(ethylphenyl) phosphite, phenyl · dicyclohexyl phosphite, phenyl · diisooctyl phosphite, phenyl · di(tridecyl) phosphite, diphenyl · cyclohexyl phosphite, diphenyl · isooctyl phosphite, diphenyl · 2-ethylhexyl phosphite, diphenyl · isodecyl phosphite, diphenyl · cyclohexylphenyl phosphite, diphenyl · (tridecyl) thiophosphite, nonylphenyl · ditridecyl phosphite, phenyl · *p-tert*-butylphenyl · dodecyl phosphite, diisopropyl phosphite, *bis*[octadecylpoly(oxyethylene)] phosphite, octylpoly(oxypropylene) · tridecylpoly(oxypropylene) phosphite, monoisopropyl phosphite, diisodecyl phosphite, diisooctyl phosphite, monoisooctyl phosphite, didodecyl phosphite, monododecyl phosphite, dicyclohexyl phosphite, monocyclohexyl phosphite, monododecylpoly(oxyethylene) phosphite, *bis*(cyclohexylphenyl) phosphite, monocyclohexyl · phenyl phosphite, *bis*(*p-tert*-butylphenyl) phosphite, tetratridecyl · 4,4'-isopropylidenediphenyl diphosphite, tetratridecyl · 4,4'-butylidene*bis*(2-*tert*-butyl-5-methylphenyl) diphosphite, tetraisoctyl · 4,4'-thio*bis*(2-*tert*-butyl-5-methylphenyl) diphosphite, *tetrakis*(nonylphenyl) · poly(propyleneoxy)isopropyl diphosphite, tetratridecyl · propyleneoxypropyl diphosphite, tetratridecyl · 4,4'-isopropylidenedicyclohexyl diphosphite, *pentakis*(nonylphenyl) · *bis*[poly(propyleneoxy)isopropyl] triphosphite, *heptakis*(nonylphenyl) · *tetrakis*[poly(propyleneoxy)isopropyl] pentaphosphite, *heptakis*(nonylphenyl) · *tetrakis*(4,4'-isopropylidenediphenyl) pentaphosphite, *dekakis*(nonylphenyl) · *heptakis*(propyleneoxyisopropyl) octaphosphite, decaphenyl · *heptakis*(propyleneoxyisopropyl) octaphosphite, *bis*(butoxy-

carboethyl) · 2,2-dimethylene-trimethylene dithiophosphite, *bis*(isooctoxycarbomethyl) · 2,2-dimethylenetrimethylene dithiophosphite, tetradodecyl · ethylene dithiophosphite, tetradodecyl · hexamethylene dithiophosphite, tetradodecyl · 2,2'-oxydiethylene dithiophosphite, pentadodecyl · di(hexamethylene) trithiophosphite, diphenyl phosphite, 4,4'-isopropylidene-dicyclohexyl phosphite, 4,4'-isopropylidene diphenyl · alkyl (C12 to C15) phosphite, 2-*tert*-butyl-4-[1-(3-*tert*-butyl-4-hydroxyphenyl)isopropyl] phenyldi(*p*-nonylphenyl) phosphite, ditridecyl · 4,4'-butylidene*bis*(3-methyl-6-*tert*-butylphenyl) phosphite, dioctadecyl · 2,2-dimethylenetrimethylene diphosphite, *tris*(cyclohexylphenyl) phosphite, hexatridecyl · 4,4',4''-1,1,3-butanetolyl-*tris*(2-*tert*-butyl-5-methylphenyl) triphosphite, tridodecyl thiophosphite, decaphenyl · *heptakis*(propylene-oxyisopropyl) octaphosphite, dibutyl · *pentakis*(2,2-dimethylenetrimethylene) diphosphite, dioctyl · *pentakis*(2,2-dimethylenetrimethylene) diphosphite, didecyl · 2,2-dimethylene-trimethylene diphosphite, and lithium, sodium, potassium, magnesium, calcium, barium, zinc and aluminum metal salts thereof. These compounds may be used individually or in combinations of two or more.

[0052] The upper limit of the amount of organophosphite ester compound to be compounded is preferably 3.0 parts by weight or less, and more preferably 2.0 parts by weight or less. The lower limit is preferably 0.01 parts by weight or greater, and more preferably 0.02 parts by weight or greater. If the amount to be compounded is less than 0.01 parts by weight, the effect of inhibiting heat degradation during working will become difficult to obtain, while if the amount exceeds 3.0 parts by weight, the effects that minimize heat degradation will be excessive, which is not economically advantageous.

[0053] It is preferable to use a combination of a phenolic antioxidant and an organophosphite ester compound in order for the heat degradation-inhibiting effect to be further enhanced.

[0054] In the present invention, the tensile storage modulus of the polyester resin composition is preferably 10^7 Pa or higher at 25°C, and 10^7 Pa or lower at temperatures below 180°C. In the region at or below 250°C, the temperature region where the modulus ranges from 10^7 Pa to 10^6 Pa is preferably 60°C or higher. A modulus of less than 10^7 Pa at 25°C is inappropriate for applications as a vinyl chloride sheet substitute, which is the object of the invention. Keeping the temperature region at 60°C or higher enables the appropriate viscoelasticity to be maintained in response to the distribution or variation in calender temperature control during calendering. The

appropriate viscoelasticity may be attained during calendering by means of compounding an appropriate amount of crystalline polyester with the amorphous polyester. The level may also be adjusted according to the amount of crystal-nucleating agent or lubricant added. The tensile storage modulus is obtained by means of using a dynamic viscoelasticity measurement device to assess a resin in the form of a sheet. Typically, the sample sheet is 15 mm long (not including the gripping length), 4 mm wide, and approximately 1 mm thick, and the conditions for measurement involve fixing the frequency at 10 Hz and scanning the sheet at a temperature elevation rate of 20°C/min from -20°C until measurement becomes impossible (a maximum of 250°C). There are no particular requirements specified for the method used to fabricate the sample sheet, but a smooth sheet may be obtained by means of sandwiching the polyester resin between polyimide films or other highly heat-resistant films, and then using a heat press or similar device set to a temperature at least 10°C higher than the softening point of the polyester resin to compress the assembly.

[0055] Other components may also be suitably added to the polyester resin composition of the present invention according to the application. Examples of such components include fillers, UV absorbers, photostabilizers, pigments, antistatic agents, antibacterial agents, epoxy compounds, crosslinking agents, and sulfur-based antioxidants.

[0056]

[Working Examples] The present invention is described in detail below with reference to working examples; however, the present invention shall not be construed to be limited to these examples.

[0057] The measurement values described in the synthesis examples were obtained according to the following methods.

[0058] Polyester composition: The resin was dissolved in heavy chloroform and determined according to H^1 -NMR.

[0059] Glass transition point and melting point: A differential scanning calorimeter was used, and 10 mg of a measurement sample was introduced into an aluminum pan, which was then covered and sealed. Measurements were made at a temperature elevation rate of 20°C/min.

[0060] Number-average molecular weight: Determined as a value converted for polystyrene by means of gel permeation chromatography, using hexafluoroisopropanol as a solvent.

[0061] Acid value: Determined by means of dissolving the resin in chloroform and performing titration with a 0.1 N potassium hydroxide ethanol solution. Phenol phthalein was used as the indicator.

[0062] Storage modulus: A sample of the polyester resin composition was placed on a tabletop heat press adjusted to 200°C, with a polyimide film ("Capton"; manufactured by DuPont-Toray Co., Ltd.) interposed therebetween. The sample was held in place for 20 sec under a pressure of 2 N/mm², resulting in a 1 mm-thick sheet sample. The sample was cut to a length of 15 mm (not including the gripping length) and a width of 4 mm, then positioned in a dynamic viscoelastometer ("DVA-200"; manufactured by I.T. Keisoku Seigyo). The measurements were performed in tensile mode. The conditions for measurement involved fixing the frequency at 10 Hz and scanning the sample at a temperature elevation rate of 20°C/min from -20°C until measurement became impossible (a maximum of 250°C).

[0063] Example detailing the synthesis of amorphous polyester (A)

960 weight parts of dimethyl terephthalate, 527 weight parts of ethylene glycol, 156 weight parts of neopentyl glycol, and 0.34 weight parts of tetrabutyl titanate were added into a reaction vessel fitted with a stirrer, temperature gauge, and distillation cooler, and transesterified for two hours at 170 to 220°C. Once transesterification was complete, the reaction system temperature was elevated from 220 to 270°C, while the pressure inside the system was gradually reduced, until a level of 500 Pa had been attained after 60 min. Polycondensation was subsequently performed for 55 min at 130 Pa or less to obtain amorphous polyester (A).

[0064] Amorphous polyester (A) was analyzed using NMR, which revealed a composition in which the dicarboxylic acid component was 100 mol% terephthalic acid, and the diol component was 80 mol% ethylene glycol and 20 mol% neopentyl glycol. The glass transition point was 78°C, the number-average molecular weight was 28000, and the acid value was 30 eq/10⁶ g.

[0065] Amorphous polyesters (B) through (E) were manufactured in the same manner as amorphous polyester (A). The compositions and measurement results are all shown in Table 3 (the numerals refer to mol% in the resin).

[0066] Crystalline polyesters (a) through (e) were manufactured in the same manner as amorphous polyester (A). The compositions and measurement results are all shown in Table 3 (the numerals refer to mol% in the resin).

[0067]

[Table 3]

| | | Synthesis examples | | | | | | | |
|---------------------|---|----------------------|-------|-------|-------|------------------------|-------|-------|-------|
| | | Amorphous polyesters | | | | Crystalline polyesters | | | |
| | | A | B | C | D | a | b | c | d |
| Acid | Terephthalic acid | 100 | 88 | 90 | 100 | 63 | 65 | 68 | 80 |
| | Isophthalic acid | | | 10 | | 10 | | 32 | 20 |
| | Adipic acid | | 12 | | | 27 | 35 | | |
| Glycol | Ethylene glycol | 80 | 78 | 72 | 71 | | 35 | | 100 |
| | Neopentyl glycol | 20 | | | | | | | |
| | 2-Methyl-1,3-propanediol | | 22 | | | | | | |
| | 1,3-Propanediol | | | 28 | | | | | |
| | 1,4-Cyclohexanedimethanol | | | | 29 | | | | |
| | 1,4-Butanediol | | | | | 100 | 64 | 93 | |
| | 1,6-Hexanediol | | | | | | | | |
| | Polytetramethylene glycol (molecular weight: 1000) | | | | | | 1 | 7 | |
| Physical properties | Number-average molecular weight | 28000 | 25000 | 33000 | 29000 | 18000 | 26000 | 34000 | 25000 |
| | Glass transition temperature (°C) | 78 | 55 | 58 | 78 | -6 | -9 | -32 | 70 |
| | Melting point (°C) | | | | | 160 | 135 | 142 | 198 |
| | Acid value (eq/10 ⁶ g) | 30 | 16 | 38 | 25 | 28 | 30 | 32 | 15 |

[0068] The polyesters shown in Table 3 were mixed in a beaker with each of the components shown in Tables 4 and 5, and the resulting mixtures were kneaded on two 6-inch chilled rolls that had been set to 180°C. The mixing was performed while any resin that had adhered to the chilled rolls was periodically removed with a spatula. Measurements were taken of the time of adhesion from the time mixing started, taking the time the resin could not be peeled off any longer as the time at which the resin became adhered to the roll. Kneading was performed for a further five minutes, after which the gap between the rolls was set to 0.3 mm (i.e., the sheet thickness was set to 0.3 mm) to obtain a sheet. The results are shown in Tables 4 and 5. The occurrence of resin sag was assessed by assigning "A" (no resin sag; smooth sheet obtained) or "B" (resin sag occurred; sheet of uniform thickness not obtained) to the state of sheet takeoff. These results are shown in Tables 4 and 5 together with the storage moduli of the resulting sheets.

[0069] The crystal-nucleating agents, lubricants, and stabilizers cited in Tables 4 and 5 are identified as follows.

I: Sodium stearate

II: Zinc salt of tridecyl poly(oxyethylene)phosphate

III: Styrene-modified polyethylene wax

IV: *Tris*(3,5-*di-tert*-butyl-4-hydroxybenzyl)isocyanurate

[0070] All figures for the amounts of polyesters, crystal-nucleating agents, lubricants, and stabilizers in the tables are in parts by weight.

[0071]

[Table 4]

| | | Working Examples | | | | | | | | | | |
|--------------------------|---|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Amorphous polyester | A | 90 | 86 | 78 | | | | | | | 93 | 80 |
| | B | | | | 80 | | | | | | | |
| | C | | | | | 88 | | | | | | |
| | D | | | | | | 93 | 85 | 88 | 100 | | |
| Crystalline polyester | a | 10 | 14 | 22 | | 5 | | 15 | | | | |
| | b | | | | | | 7 | | | | | |
| | c | | | | 20 | 7 | | | | | 7 | |
| | d | | | | | | | | 12 | | | 20 |
| Crystal-nucleating agent | I | 1 | 0.2 | 1 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 1 |
| Lubricant | II | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| | III | | | 0.5 | | | | | | | 0.5 | 0.5 |
| Stabilizer | IV | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Evaluation | Adhesion time (min) | 18 | 22 | >30 | 27 | 24 | 11 | 10 | 13 | 15 | >30 | >30 |
| | Resin sag | A | A | A | A | A | A | A | A | A | A | A |
| | Elastic modulus temperature width ¹⁾ | 60 | 60 | 65 | 60 | 60 | 60 | 60 | 60 | 50 | 60 | 90 |
| | Transparency | 4 | 4 | 5 | 4 | 4 | 4 | 4 | 4 | 4 | 5 | 5 |
| | Solvent resistance | 5 | 4 | 5 | 5 | 5 | 4 | 4 | 4 | 4 | 4 | 5 |

*1) The elastic modulus temperature width refers to the width of the temperature region where the tensile storage modulus ranges from 10^7 Pa to 10^6 Pa.

[0072]

[Table 5]

| | | Comparative Examples | | |
|--------------------------|-----------------------------------|----------------------|-----|-------------------|
| | | 1 | 2 | 3 |
| Amorphous polyester | A | 90 | 100 | |
| | D | | | |
| Crystalline polyester | a | 10 | | |
| | c | | | |
| | d | | | 100 |
| Crystal-nucleating agent | I | 1 | | |
| Lubricant | II | | 1 | 1 |
| | III | | | |
| Stabilizer | IV | | | 0.3 |
| Evaluation | Adhesion time (min) | 0 | 24 | >30 ¹⁾ |
| Evaluation | Resin sag | — | B | — |
| | Elastic modulus temperature width | — | 45 | — |
| | Transparency | — | 4 | — |
| | Solvent resistance | — | 1 | — |

*1) Did not dissolve; sheet could not be formed

[0073] The transparency and solvent resistance data recorded in the tables were measured according to the following methods.

[0074] Transparency: sheets were compared macroscopically and evaluated according to the following levels.

- 5: high transparency
- 4: good transparency
- 3: transparent

- 2: slightly non-transparent
- 1: somewhat non-transparent

[0075] Solvent resistance: Sheets were immersed in methyl ethyl ketone for ten minutes, after which macroscopic observations were used to determine whether the sheets had whitened or swelled. The assessment levels were as follows:

- 5: no change
- 4: appreciable degree of swelling, but no major change
- 3: whitening
- 2: whitening; some swelling on the surface
- 1: whitening; surface dissolved

[0076] The presence of a "-" mark in the transparency or solvent resistance columns of the comparative examples signifies that adhesion occurred, and that it was impossible to produce a sheet.

[0077]

[Effect of the Invention] As has been described in the foregoing, the polyester resin composition of the present invention is a combination of an amorphous polyester, crystal-nucleating agent, and lubricant, with a crystalline polyester further added thereto. This combination accordingly makes it possible not only to calender polyester resin compositions (and to prevent resin sag, in particular) in a simple manner, which has hitherto been problematic, but also to calender sheet that has exceptional quality as relates to solvent resistance and detergent resistance, and possesses satisfactory transparency when finished.